

The Use of Contaminant Transport Models at the RFETS

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Introduction. The Actinide Migration Evaluation (AME) group was established to provide guidance on issues of actinide behavior and mobility in surface water, groundwater, and soil environments. The AME group draws on the state-of-the-art understanding in the scientific communities of actinide chemistry, geochemistry, migration, soil erosion, and sediment and contaminant transport processes. This knowledge is used to help characterize current environmental conditions at RFETS and recommend a path forward for Site personnel for long-term protection of surface water quality during and after Site closure. The AME group has developed a set of urgent, near- and long-term goals that include (i) addressing actinide migration concerns of importance to the Site, (ii) development of an understanding of environmental actinide migration mechanisms in light of recent surface water exceedences, (iii) evaluation of the impacts of actinide migration on remedial actions, (iv) assessing the protection of soil action levels for surface water quality, and (v) assessing actinide migration in terms of long-term surface water compliance at Site closure and potential down-stream impacts.

Adsorption Models and Contaminant Transport Modeling. Assessment of chemical risk due to subsurface contaminants, and the cost of remediation depends critically on the models that predict contaminant breakthrough times and concentrations to specific targets; drinking water wells, surface water bodies, and/or geographical boundaries to a contaminated site. For systems where contaminant partitioning is dominated by chemical equilibria, a rigorous approach to surface and solution speciation (based on sound chemical thermodynamic principles) will provide a reliable description of contaminant chemistry. (I. Grenthe, I. Puigdomenech, Eds., "Modeling in Aquatic Chemistry", Nuclear Energy Agency, OECD-OCDE, 1997).

For systems where equilibrium conditions exist, a variety of adsorption models, from simple distribution coefficients (K_d) to more sophisticated electrostatic adsorption models have been used for contaminant transport modeling. The most commonly used adsorption model in contaminant transport calculations is the distribution coefficient, or K_d model. In large part this reflects the simplicity of including a K_d value in a transport calculation (Stumm 1992). As with any model, the simple K_d model has a set of well-defined boundary conditions under which it can be used properly.

The distribution coefficient, K_d , is the ratio of the mass of solute species adsorbed or precipitated on the solids per unit of dry mass of the soil, C_s , to the solute concentration in the liquids, C_l . The distribution coefficient represents the partition of the solute in the soil matrix and soil water, assuming that *equilibrium* conditions exist between the soil and solution phases. A linear Freundlich isotherm, which assumes complete reversibility of ion adsorption, has been extensively used to correlate the relationship between C_s and C_l . These distribution coefficients take the form:

$$K_d = C_s/C_l \text{ (L kg}^{-1}\text{)}$$

Where C_s is the concentration of the solid particles (mol kg⁻¹) and C_l is the concentration in liquid (mol L⁻¹). K_d values, therefore, typically have units of mL/g or L/kg. The transfer of contaminants from the liquid to the solid phase or vice versa may be controlled by mechanisms such as adsorption, ion exchange, precipitation, chemical reaction, etc. depending on the identity of the contaminant and the solid. For *soluble* contaminant species it is generally observed that as the concentration of the contaminant increases, the amount sorbed to a contacting solid also increases. This behavior is typical of trace organic and inorganic substances that are *soluble* in aqueous media. It is important to recognize that the K_d model assumes that the contaminant is a *soluble* species such as a pesticide (organic) or a dissolved metal cation (Sr²⁺, UO₂²⁺, etc.), and that equilibrium conditions exist between the solid and solution phases. For *soluble* species, where K_d values dominantly reflect reversible sorption processes, then K_d values can be used to model the removal of contaminants from by soils and sediments. This is the premise under which the RESRAD (RESidual RADioactivity) modeling program was developed, where, indeed, it should be applicable to problems associated with *soluble* contaminant species with *reversible* sorption/desorption processes. The fundamental boundary conditions for the K_d model are therefore “soluble” species and “reversible” equilibria. In order to assess the applicability of the K_d model, we must assess whether the actinide ions satisfy these fundamental assumptions.

Basic Actinide Environmental Behavior. Extensive field observations and research have been conducted in the U.S. and internationally on the environmental behavior of actinide elements in very diverse sets of environments over the past 30-40 years. This has provided a rather good base for understanding of the major types of species and their transport mechanisms in soils and natural waters.

In natural waters plutonium solubility is limited by the formation of amorphous $\text{Pu}(\text{OH})_4$ or polycrystalline PuO_2 . A reasonable estimate for the solubility product (K_{sp}) of $\text{Pu}(\text{OH})_4$ is approximately 10^{-54} , which approaches 10^{-64} as the amorphous $\text{Pu}(\text{OH})_4$ ages to crystalline PuO_2 . This estimate puts an upper limit on the amount of *dissolved* (i.e. ionic/molecular) Pu that can be present, even if higher oxidation states such as Pu(V) or Pu(VI) are the more stable solution forms. Pu(V) has a low tendency to hydrolyze and form complexes with ligands, and is much less likely to be sorbed to solid surfaces and colloidal particles than the other oxidation states of plutonium. While PuO_2 has a laboratory measured solubility range of 10^{-10} - 10^{-13} M, the total concentrations of plutonium observed in short laboratory studies, however, are usually in the range 10^{-8} - 10^{-9} M, and limited by the formation of the highly insoluble amorphous $\text{Pu}(\text{OH})_4$ (Knopp, R. et al. *Radiochim. Acta* 1999, 86, 101). Moreover, in many natural waters, actual Pu concentrations are often on the order of 10^{-15} M (similar to global fallout) and these low values may be traced to sorption processes. Sorption of hydrolyzed Pu(IV) in natural water on mineral surfaces and surfaces coated with organic material is accountable for the very low observed concentrations of dissolved Pu even in the absence of $\text{Pu}(\text{OH})_4$ (am) or PuO_2 (c). The strong tendency of $\text{Pu}(\text{OH})_4$ to sorb onto surfaces is a dominant and often controlling feature in plutonium geochemistry. Due to the very low solubility of Pu(V)/Pu(IV), and the tendency of Pu(IV) to adhere to organic and mineral particles, the primary path of Pu transport is usually migration of colloidal particles to which Pu(IV) is sorbed. Indeed, when concentrations above fallout levels of Pu are observed, they have generally been linked to colloids and particulates (Kersting, A. B. et al., *Nature*, 1999, 397, 56). Analysis of Pu in samples from RFETS does confirm that particulates are the predominant mode of transport at concentrations above fallout levels (Santschi, P. et al. 2000).

By contrast to plutonium, uranium has less redox activity and is generally present in natural and sea waters as soluble uranium(VI) complexes. In surface waters or waters in soils of carbonaceous material, uranium(VI) is present as $\text{UO}_2(\text{CO}_3)_n^{2n-2}$ ($n = 1-3$). Only in reducing waters is uranium(IV) present, and uranium(IV) has an insignificant role in natural waters. Uranium(IV) is therefore very similar to plutonium(IV) in its solubility properties. Americium exists only in the trivalent state and can be present environmentally, as complexed species (eg. $\text{Am}(\text{OH})_n^{2-n}$, $\text{Am}(\text{CO}_3)^+$, $\text{Am}(\text{OH})(\text{CO}_3)^0$, etc.) and sorbed to colloids. Thus its behavior can resemble that of uranium or plutonium, depending on the pH and the anions present in the water of the particular environment.

Environmental Chemistry Issues – Plutonium/Americium. The data amassed during the AME studies is consistent with our expectations of plutonium and americium chemical behavior in

the environment. The data indicate that plutonium and americium in RFETS surface waters have extremely low concentrations, in the femtomolar (10^{-15} M) range, similar to global fallout. Site-specific studies indicate that reducing conditions do not remobilize plutonium, and that the bulk of plutonium and americium is associated with small ($< 2\mu\text{m}$) colloidal particles that readily settle in pond water. These results are consistent with the known chemical behavior of plutonium(IV) and americium(III). Extended X-ray Absorption Fine Structure (EXAFS) studies show unambiguously that plutonium in soils taken from the 903 Pad is in oxidation state (IV), in the chemical form (speciation) of insoluble PuO_2 . This is significant in that it had been widely held at the Site that the chemical form of plutonium was the dioxide, but this had never been proven. The identification of Pu(IV) in the chemical form of PuO_2 is consistent with the observed insolubility of Pu in site-specific waters. Furthermore, the data clearly indicate that physical (particulate) transport is the dominant mechanism for Pu migration at RFETS. This recognition has identified the need for an erosion model, and that for plutonium, transport models based on the K_d approach and assuming dissolved (molecular) Pu species are inappropriate and not scientifically defensible.

Environmental Chemistry Issues – Uranium. Leakage of liquid wastes from the Solar Ponds has produced a contaminant plume characterized by high concentrations of nitrate and uranium. For the uranium plume, important questions have been raised as to the contribution of naturally occurring uranium relative to uranium from waste and as to the processes affecting uranium mobility such as mineral solubility control. Uranium isotopes (235, 236, and 238) were measured from a few wells to help identify natural vs. anthropogenic sources. Indications of both depleted and enriched uranium with measurable ^{236}U were obtained from the Solar Ponds Plume (SPP) whereas background (uncontaminated) wells were found to have non-detectable ^{236}U and natural activity ratios of $^{235}\text{U}/^{238}\text{U}$. However, as the sampling was limited in scope at the SPP and there is still some possibility of natural uranium contributions in the SPP area. Mixtures of depleted and enriched uranium could occur with little or non-detectable ^{236}U to give the appearance of naturally occurring material. Sampling and isotopic measurements have to date confirmed that uranium isotope systematics can be used to differentiate natural from anthropogenic uranium sources and that both sources exist at RFETS although the extent of natural source material at SPP is unclear. Further measurements are currently underway that should reduce this uncertainty.

A geochemical modeling investigation on the potential for mineral solubility control on uranium mobility has shown that ground waters in the SPP are undersaturated with respect to all U(IV) and U(VI) minerals for which reliable thermodynamic data exist. These results would suggest that uranium should be relatively free to move with the ground water unless attenuated. The fact that the uranium plume as mapped appears distinctly attenuated compared to the nitrate plume

suggests four possibilities for attenuation: (1) sorption processes, (2) capillary movement into the vadose zone during dry periods forcing mineral precipitation, (3) uranium precipitated immediately beneath the SPP as leaking solutions reacted with the aquifer material, and (4) a significant fraction deposited in the pond sludge during evaporation. The tendency for the highest uranium concentrations to be spatially located close to the Solar Ponds (unlike the nitrate) and the tendency for all the ground waters to be undersaturated with respect to uranium mineral solubilities suggests that the third possibility, uranium precipitation in or beneath the SPP and a slow rate of dissolution, is likely. The potential occurrence of elevated uranium in the soils and sediments beneath the SPP needs to be determined because it could have a major influence on the remediation activities for the SPP.

Dissolved species versus particulate transport at RFETS. Since all the data amassed indicate that plutonium is present as insoluble plutonium oxides and migration occurs via colloidal/particulate transport, transport-modeling calculations (*e.g.* programs such as RESRAD run with conventional options) that assume soluble forms and the existence of equilibrium conditions between soil and solution phases of plutonium are of no value for assessing the risk of plutonium exposure at RFETS. The author of the RESRAD program (Dr. Charley Yu, Argonne National Laboratory) is well aware of this limitation, and has discussed it with members of the AME Advisory Group. Moreover, the user documentation of the RESRAD model (section 32.3) recognizes this caveat and deficiency in using K_d 's for materials that are insoluble, and includes an optional approach that accepts input of the solubility limit of relatively insoluble solids so that the program can derive an *effective distribution coefficient* for use in the calculation. This effectively turns off the sorption, and allows for solubility to control the release of the insoluble contaminant. While this approach is an improvement over the practice of using a K_d value for plutonium from the literature, it is still not appropriate for use with plutonium to assess the risk to public health at RFETS.

All data indicate that particulate transport is the dominant migration pathway for plutonium in RFETS soils and surface runoff. The RESRAD program also contains a module that incorporates erosion rates estimated by means of the Universal Soil Loss Equation (USLE), an empirical model that has been developed for predicting the rate of soil loss by sheet and rill erosion. This estimation approach is probably appropriate for soluble contaminants, where erosion represents only a minor transport pathway relative to sorption-desorption processes. Since erosion was identified as the dominant transport path for plutonium in soils at RFETS, financial and manpower resources have been devoted to the development of scientifically defensible erosion/sediment transport models for plutonium transport at the Site. Indeed, while plutonium in soils at RFETS

is relatively insoluble, uranium on the other hand is prone to formation of soluble compounds. Therefore, uranium has a higher probability of aqueous dissolved transport, and dissolved species transport calculations such as RESRAD are useful for risk assessment of uranium contamination at the Site. A thorough understanding of the uranium geochemistry, the uranium source-term, and the overall water balance at the Site are of great importance with respect to uranium transport calculations. For uranium therefore, the application of models such as RESRAD for risk assessment, and the application of more sophisticated geochemical models are both more useful and scientifically defensible.

Recommendation on the Use of K_d values at RFETS. The use of K_d values to assess the migration and hence the risk of exposure to uranium at RFETS is justified based on our understanding of the geochemical behavior of *uranium* at RFETS. Therefore, models such as RESRAD are defensible for uranium risk assessment. However, it is the expert judgement of the AME Advisory Group that the use of K_d values to assess migration and hence risk of exposure to *plutonium* at RFETS is not scientifically acceptable and not defensible legally.

General concerns. There still seems to be an ongoing problem with understanding the limitations of K_d values (by the users of the RESRAD model at RFETS) as a universal model for contaminant reactivity and transport, particularly as applied to RFETS. The RESRAD program was developed for specific applications based on a well defined, but limited (or general) conceptual model for contaminant transport mechanisms, and when used with a full understanding of the input parameters, and the inherent limitations of the model, it can be an effective tool for assessing risk to public health and radiation dose. The authors of the program have worked hard to make this program user friendly, and therefore accessible to a wide audience. We caution however, that any computational model is only as good as the conceptual model, the input parameters, and the knowledge and experience of the user. Our concern about the use of RESRAD for plutonium migration at RFETS has more to do with the approach, and apparent willingness of the end-users to utilize broad generalizations for chemical behavior. A case in point is the continued insistence that the AME advisors offer a K_d value for plutonium in spite of our current scientific understanding of plutonium behavior at RFETS. A K_d is of little value for plutonium as it cannot be used in RESRAD since the assumption of a molecular sized soluble species of Pu is scientifically incorrect at RFETS.